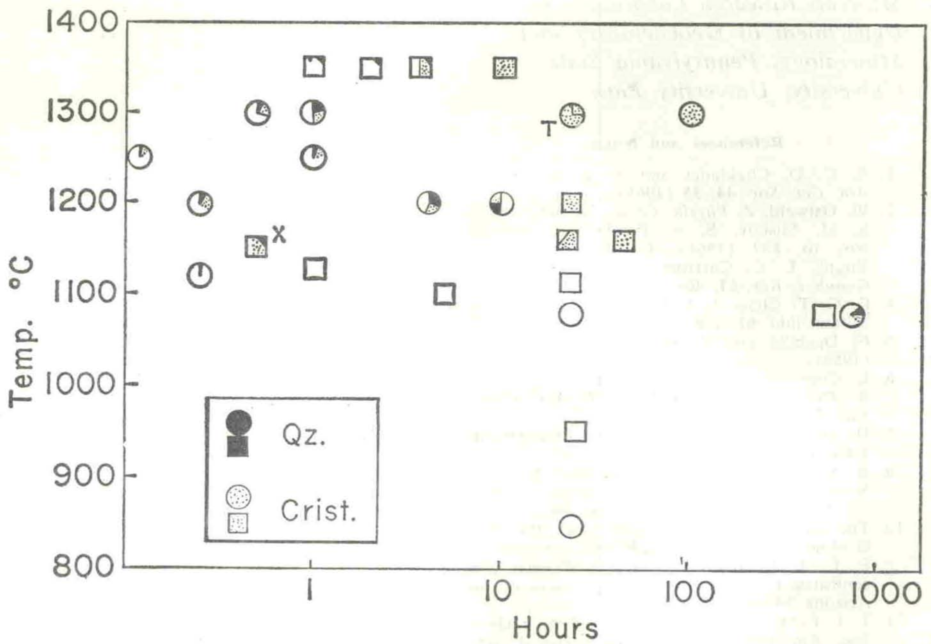

Fig. 1. Influence of time and temperature on the alteration of coesite. Time is plotted on a logarithmic scale. Solid and dotted filling indicate relative amounts of quartz, cristobalite, and tridymite modifications determined by x-ray diffraction. Circle and square points are for separate lots of concentrated coesite in which grain sizes averaged 8 and 17 microns respectively. The square marked X represents the average observations during a 5-hour x-ray study at high temperature.

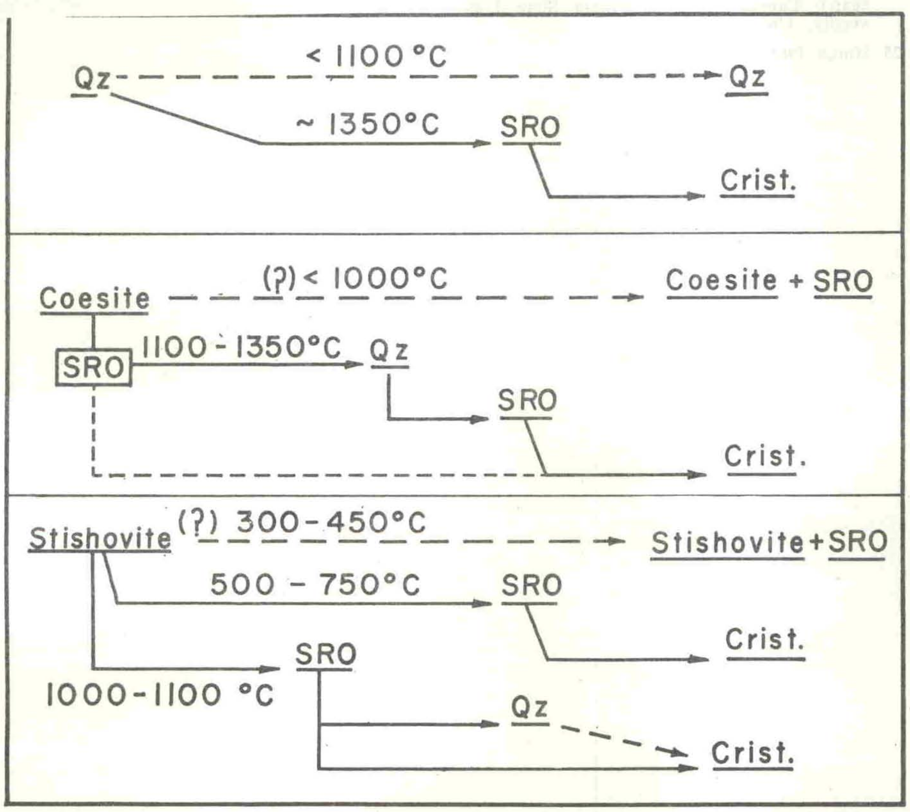

Fig. 2. Scheme of the most likely inversion paths of coesite and stishovite. Lower temperature limits are strongly dependent on time.

The data in Table 2 show that the stishovite differs markedly from the coesite in metastable persistence. It withstands exposure at 425°C for a few hours, but becomes completely amorphous to x-ray diffraction methods after heating less than 5 minutes between 650° and 750°C. Judging from the change of the aggregate refractive index, stishovite breaks down slowly at 350°C and much faster at 425°C. At lower temperatures the stishovite should be more resistant to change, obvious in its persistence in the crushed sandstone of the Arizona Meteor Crater formed thousands of years ago. At higher temperatures and longer heating times (½ to 18 hours) crystallization of quartz (in the stability field of tridymite) in the presence of the SRO phase is again observed. Although cristobalite is the first to be observed by x-ray diffraction it is barely evident microscopically after 18 hours at 1100°C whereas quartz can be detected microscopically after 2 hours. No evidence of a transient formation of coesite from the much denser stishovite has as yet been found.

In Fig. 2, we attempt to summarize schematically some of the results obtained and to offer a probable interpretation. Coesite apparently forms a "dense," fine grained SRO phase, which then is converted to quartz. In the case of stishovite it is inconceivable that the rutile-type structure (where the coordination number is 6) could avoid the SRO stage and indeed there is direct evidence for the formation of the SRO and subsequent conversion at low temperatures. That the refractive index of the SRO phase rapidly approaches that of silica glass, may be a manifestation of a high disordering tendency of the coordination change, not involved in the case of coesite. The relative amounts of the various phases formed in any particular run might be explained on the basis of the competing reactions stishovite (or coesite) → SRO, SRO → quartz, quartz → SRO, and SRO → cristobalite with widely differing activation energies (*12*).

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Table 2. Heat treatment of stishovite at 1 atm pressure. The bulk color of the samples changed from grey to white with the presence of a large amount of amorphous material. A, amorphous, C, cristobalite, Q, quartz, S, stishovite, W, weak. For comparison, data from the literature is included. *a*. Synthetic stishovite of Stishov and Popova [*Geokhimiya* No. 10, 837 (1961)]. *b*. Natural stishovite, Fahey (*11*).

Temp. (°C)	Time (hr)	Results: X-ray	Microscopy	R.I. aggregate*
1100	18	C + Q	Q + A + C	—
1100	2	C + Q	Q + A + C	—
1060	0.5	C	A	1.456
1040	0.1	A	A	1.456
750	0.1	A	A	1.480
750	0.2	A	A	—
650	0.2	W S	S	1.500
500	0.2	S	S	—
425	3.5	S	S	1.740
350	70.	S	S	1.783
350	0.2	S	S	—
130	0.5	S	S	—
900 (*a*)	6.0	C + A		—
498 (*b*)	165.	A + S		1.557

* R.I. of starting stishovite aggregate (1.793 average).

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12. This work is part of a program of high pressure crystal chemical studies supported by the Metallurgy Branch of the Office of Naval Research. We are indebted to N. Raimondo who performed many of the coesite experiments. This report is contribution No. 62-47, College of Mineral Industries, Materials Research Laboratory, Pennsylvania State University, University Park.

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